THE CUPROUS CHLORIDE ELECTRODES

BY RALPH F. NIELSEN[1] AND DENTON J. BROWN

The Copper Amalgam–Cuprous Chloride Electrode

Introduction

The copper-cuprous chloride electrode has been measured by Immerwahr,[2] by Luther and Wilson,[3] and by Noyes and Chow.[4] These investigations are subject to the errors of not using a reproducible form of copper, of not preparing the electrodes in the absence of oxygen and of not rotating the electrodes to insure equilibrium. Luther and Wilson employed the cell Cu, CuCl(s), KCl($N/20$), N. E. Noyes and Chow employed the cell Cu, CuCl(s), HCl, H_2. Immerwahr used the cell Cu, CuCl(s), $KNO_3(N)$ + HCl($N/20$), N. E., in which the complete cell reaction is obviously doubtful.

In our work we first used the cell Cu(amalgam), CuCl, HCl, HgCl, Hg, since it has the advantage of having an electromotive force practically independent of concentration. We tried to follow the method of Ellis[5] in preparing the calomel electrodes, since he obtained results which varied only a few hundredths of a millivolt. This was essentially the electrolytic method of Hulett.[6] We were, however, unable to obtain constant values, and when we rotated the calomel electrodes for a day or two, as he recommends, we obtained values which were nearly ten millivolts too high, as indicated by comparison with hydrogen electrodes. The same results were obtained with a second preparation of electrolytic calomel. For this reason we employed the cell Cu(amalgam), CuCl(s), HCl, H_2.

Apparatus and Solutions

The copper amalgam was the same two-phase electrolytic amalgam as that described in our previous paper on the potential of copper.[7] Cuprous chloride was prepared directly in the electrode vessel by addition of a solution of chloro-cuprous acid to water, while a stream of purified nitrogen bubbled through the vessel. The chloro-cuprous acid was prepared by reduction of a hydrochloric acid solution of cupric chloride

[1] This paper is taken from part of a thesis submitted by Ralph F. Nielsen for the degree of Doctor of Philosophy at the University of Nebraska. The problem of the determination of the free energies of copper compounds was selected by him at the suggestion of Professor Merle Randall of the University of California and this paper represents the work on the copper chlorides.

[2] Immerwahr, *Z. Electrochem.*, **7**, 477 (1900).

[3] Luther and Wilson, *Z. physik. Chem.*, **34**, 488 (1900).

[4] Noyes and Chow, THIS JOURNAL, **40**, 739 (1918).

[5] Ellis, *ibid.*, **38**, 737 (1916).

[6] Hulett, *Phys. Rev.*, **32**, 321 (1900).

[7] Nielsen and Brown, THIS JOURNAL, **49**, 2423 (1927).

with copper. The amalgam, the supply of which was always kept under an acidified copper sulfate solution, had been previously put in the vessel after being washed. The glass stopper was then inserted and the solution brought to the proper concentration by repeatedly forcing out the solution with nitrogen and drawing in a solution of the required concentration. After drawing in each fresh supply, nitrogen was bubbled through the cell for a short time and the cell was shaken a few times. The solutions were often kept at about 40° to insure larger crystals and more rapid settling of the salt, but this seemed to have no influence on the results. The last addition of the solution was always below 25° so as to avoid any inrush of solution into the vessel when the stopcocks were opened for the potential measurements. The electrode was rotated in the thermostat four or five hours before being measured. Longer periods did not change the potential.

The hydrogen electrode consisted of a piece of platinized platinum foil. The electrode was prepared from clean platinum foil by electrolysis of a solution of pure chloroplatinic acid containing one per cent. of platinum. A four-volt battery was used and the current reversed every few minutes for one hour, as recommended by Ellis. The hydrogen entered the electrode vessel at the bottom and escaped through a trap. The platinum foil was only partially submerged in the solution. Hydrogen was prepared by electrolysis of sodium hydroxide solution and was passed through sulfuric acid before entering the preliminary washer which adjoined the electrode vessel in the thermostat and contained the same solution as the electrode vessel. Rubber connections were kept at a minimum and whenever they were used they were paraffined. In one of our measurements two hydrogen electrode vessels were used, the one receiving electrolytic hydrogen and the other hydrogen prepared from zinc and hydrochloric acid. The hydrogen from the latter source was passed through concentrated potassium hydroxide and over phosphorus pentoxide before entering the preliminary vessel. The difference in potential between the two electrodes was less than 0.01 millivolt. The hydrogen and cuprous chloride electrodes were joined through a beaker of the given solution, the arm of the cuprous chloride vessel having been protected by a plug during rotation in the thermostat. Both electrodes were set up four or five hours before being measured.

The hydrochloric acid solutions were made up from conductivity water, and weighed quantities were standardized with barium hydroxide, which in turn had been standardized with benzoic acid. Checks were obtained in all the titrations. All other apparatus and manipulations were the same as in our previous paper, such as "Type K" potentiometer, calibrated standard cell, thermostats, etc.

Electromotive Force of the Copper Amalgam Hydrogen Cell

In the following table the first column gives the number of the experiment, the second the molality of the acid used (moles per kilogram of water), and the third the partial pressure of hydrogen after correcting the

TABLE I

THE ELECTROMOTIVE FORCE OF THE CELL

Cu (in two-phase amalgam) + CuCl(s), HCl, H_2 at 25°

No.	m_{HCl}	P_H	E	γ_{HCl}
1	0.02029	700	−0.33615	0.893
2	.02029	689	− .33592	
3	.00757	695	− .38250	.933
4	.00757	698	− .38248	
5	.03564	697	− .30830	.874
6	.03564	692	− .30805	

barometer reading for temperature and subtracting the vapor pressure of the solutions, assumed equal to that of water. The fourth column gives the observed electromotive force and the fifth column the activity coefficient for the given molality of acid, interpolated from the table of Lewis and Randall.[8]

All six measurements were obtained in succession. The close agreement of each pair seems to be a fair check on the experimental work. Calculations based on these measurements will appear in the theoretical discussion.

Study of the Cell CuCl(s), CuCl$_2$(aq.), Cl$_2$(g)

Introduction.—This is of course the only combination of electrodes which we could use if we wish to avoid liquid junctions, since copper or mercury would cause precipitation of cuprous chloride from the cupric chloride solutions. The CuCl-CuCl$_2$ electrode was studied by Luther and Wilson,[8] who measured the cell CuCl, CuSO$_4$ and KCl (each $MV/20$), N. E. Obviously we cannot use this measurement in our calculations.

Experimental Work.—With the exception of the preparation of the chlorine electrodes, all procedure was the same as given above, including preparation and rotation of the CuCl-CuCl$_2$ electrodes. In setting up the chlorine electrodes we followed essentially the method of Lewis and Rupert.[9] The bulb of a separatory funnel was sealed into the neck of a carboy by means of de Khotinsky cement. A mixture of air and chlorine was forced into the carboy under pressure, the partial pressure of air being at least ten times that of chlorine. The air was dried before entering the carboy and the chlorine was taken directly from a cylinder. The carboy contained some calcium chloride to serve as a drying agent. The chlorine electrode vessels were essentially like the hydrogen electrode vessels described above, except that bright platinum-iridium foil was used instead of platinum black.
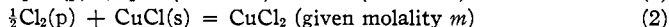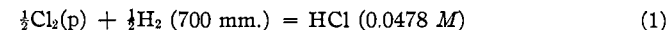
The cupric chloride solutions were made up gravimetrically. with conductivity water, from a stock solution which had been standardized iodimetrically. The stock solution had been made up from crystals of the dihydrate, obtained by recrystallization of the best c. p. product from a solution containing excess of hydrochloric acid. These crystals were dried in a vacuum desiccator containing soda-lime. The solutions were kept in Pyrex flasks, over which watch glasses had been sealed with paraffin. The saturated electrode was set up by adding excess of the dihydrated salt to the electrode vessel at the time it was set up. The more dilute solutions contained about a drop of nitric acid in 500 cc. of solution to prevent the formation of a green precipitate, probably a basic salt.

In order to standardize the chlorine mixture the stem of the separatory funnel leading from the carboy was divided by means of a Y-junction. The mixture was thus allowed to go simultaneously through one pass into an electrode vessel containing the required cupric chloride solution and through the other pass into an electrode vessel containing 0.0478 M hydrochloric acid. The hydrochloric acid electrode was measured against a hydrogen electrode with the same hydrochloric acid solution. The Cl$_2$-CuCl$_2$ electrode was measured against the CuCl-CuCl$_2$ electrode, prepared similarly to the Cu-CuCl electrodes described above. The two latter electrodes of course con-

[8] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York City, 1923.

[9] Lewis and Rupert, THIS JOURNAL, 33, 299 (1911).

tained cupric chloride of the same molality. The cells were measured almost simultaneously, after sufficient time had elapsed to insure equilibrium in all the electrode vessels. In other words, we obtained simultaneously the electromotive forces corresponding to both the following reactions

$$\tfrac{1}{2}Cl_2(p) + \tfrac{1}{2}H_2 \text{ (700 mm.)} = HCl \text{ (0.0478 } M) \qquad (1)$$
$$\tfrac{1}{2}Cl_2(p) + CuCl(s) = CuCl_2 \text{ (given molality } m) \qquad (2)$$

The data of Lewis and Rupert were then used to determine the partial pressure of the chlorine in each case. The electrodes were joined only long enough to be measured and adjustments were such as to avoid flow from one to the other.

Electromotive Force of the Cell.—In the following table the first column gives the number of the experiment, the second the molality of the cupric chloride, the third the measured electromotive force of the hydrochloric acid cell and the fourth that of the cupric chloride cell. The partial pressure of hydrogen in this series was assumed constant at 700 mm.

TABLE II

THE ELECTROMOTIVE FORCES OF THE CELL H_2 (700 mm.), HCl (0.0478 M), $Cl_2(p)$, AND THE CELL $CuCl(s)$, $CuCl_2(m)$, $Cl_2(p)$ AT 25°

No.	m_{CuCl_2}	E_{HCl}	E_{CuCl_2}
7	0.01	1.4791	1.0900
8	.01	1.4787	1.0893
9	.02	1.4812	1.0479
10	.02	1.4809	1.0476
11	.2	1.4835	.9136
12	.2	1.4745	9043
13	.2	1.4760	.9066
14	1	1.4812	.7958
15	1	1.4785	.7928
16	5.82[10]	1.4787	.6170

Calculations and Theoretical Discussion

The Copper-Cuprous Chloride Electrode

Since the reaction which occurs in the cell (Table I) is Cu (in two-phase amalgam) + H^+Cl^- (at m) = $CuCl(s)$ + $\tfrac{1}{2}H_2$ (at p), the relation between the observed e.m.f. E and that E_0 calculated for the case in which H^+, Cl^- and H_2 have unit activity is given by the expression

$$E_0 = E + 0.05915 \log \frac{(p/760)^{1/2}}{a_{H^+} \cdot a_{Cl^-}} \qquad (3)$$

in which the a's refer to the given activities. The geometric mean activity of the ions is equal to the molality m_{HCl} multiplied by the activity coefficient γ_{HCl}, provided the solubility of cuprous chloride is small, and the expression becomes

$$E_0 = E + 0.05915 \log \frac{(p/760)^{1/2}}{m^2\gamma^2} \qquad (4)$$

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[10] From the solubility measurements of Reicher and van Deventer, *Z. physik. Chem.*, **5**, 559 (1890).

The values of E_0 thus calculated are given in the third column of Table III, the first column giving the number of the experiment and the second the molality of hydrochloric acid for comparison of the data.
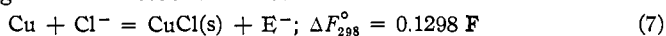
There are, however, two factors which influence the concentration of chloride ion in the hydrochloric acid solutions. The first is the formation of the complex ion $CuCl_2^-$, for which Noyes and Chow[4] found, at 25°, the relation
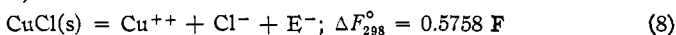
$$(CuCl_2^-)/(Cl^-) = 0.0661 \tag{5}$$

the parentheses denoting concentrations. Activities may be substituted for the concentrations in accordance with the principle[8,16] that the activity coefficient in dilute solutions is determined chiefly by the total ionic strength and is nearly the same for all ions of unit charge. In all that follows, parentheses will denote activities. The second factor is the reaction

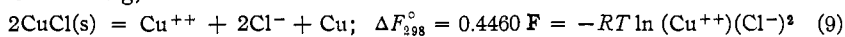$$2CuCl(s) = Cu^{++} + 2Cl^- + Cu \tag{6}$$

In the case of the most concentrated hydrochloric acid solutions (Table I), Equation 5 has a far greater effect than Equation 6 on the concentration of chloride ion. This will be evident in the subsequent calculations. Assuming that in the most concentrated solution (Cl^-) is reduced in the ratio $1/1.0661$ by complex formation, and anticipating Equation 14, we shall correct the value of E_0 for the most concentrated solution by the amount $0.828 \cdot 0.5915 \log 1.0661$ or 0.0013 volt and write[11]

$$Cu + Cl^- = CuCl(s) + E^-; \; \Delta F_{298}^\circ = 0.1298 \; F \tag{7}$$

By Equation 22,

$$CuCl(s) = Cu^{++} + Cl^- + E^-; \; \Delta F_{298}^\circ = 0.5758 \; F \tag{8}$$

Combining,

$$2CuCl(s) = Cu^{++} + 2Cl^- + Cu; \; \Delta F_{298}^\circ = 0.4460 \; F = -RT \ln (Cu^{++})(Cl^-)^2 \tag{9}$$

Then

$$(Cu^{++})(Cl^-)^2 = \text{antilog} \; \frac{-0.4460}{0.05915} = 2.82 \times 10^{-8} \tag{10}$$

If we assume that for every Cu^{++} ion produced by Equation 6, two Cl^- ions are produced, and for every $CuCl_2^-$ ion produced, one Cl^- ion disappears, then the activity of Cl^- ion in the electrode chamber is given by

$$(Cl^-) = \gamma_{Cl^-} \, m_{Cl^-} - (CuCl_2^-) + 2\gamma_{Cl^-} \cdot (Cu^{++})/\gamma_{Cu^{++}}$$
$$= \gamma_{Cl^-} \, m_{Cl^-} - 0.0661(Cl^-) + \frac{2 \times 2.82 \times 10^{-8}}{(Cl^-)^2} \times \gamma_{Cl^-}/\gamma_{Cu^{++}} \tag{11}$$

from Equations 5 and 10. We may assume that the individual ion activity coefficients are the same for all ions of unit charge and are those given in Table I. The coefficients for Cu^{++} are taken from the table of Lewis and Randall for individual ions and are given in the fourth column of Table III. The fifth column gives the solution of Equation 11. It has been assumed that all the dissolved cuprous chloride is in the form of the complex ion.

[11] The symbols and conventions used in this paper are those of Lewis and Randall, See Note 8.

Before we can correct our potentials, we must consider another effect, namely, the summation of free energies of dilution and concentration in the composition gradient portion, which occur when the cell operates and which give rise to the so-called "liquid potential." The expressions for the electromotive forces of concentration cells have been derived by integration methods,[12] and their form indicates that for convenience a sharp boundary may be assumed. Since electrical neutrality will be maintained chiefly by ions present in the largest concentration, we may assume that hydrogen ion and chloride ion are the chief substances transferred. Since the concentration of hydrogen ion is the same on both sides of the junction, the free-energy change, due to transference, accompanying the passage of one Faraday is manifested in a potential

$$\mathbf{E}_L = t_A \cdot 0.05915 \log a_1/a_2 \qquad (12)$$

where t_A is the transference number of the anion, and a_1 and a_2 are the activities of chloride ion on the two sides of the junction. If all the transference were accomplished by hydrogen ions, our values of $\mathbf{E}_0$ would have to be corrected by the amount

$$\Delta \mathbf{E}_T = 0.05915 \log \gamma m/(Cl^-) \qquad (13)$$

since all the chloride ion formed would be at activity (Cl^-) rather than at γm. The effect of Equation 12 is to offset in part that of Equation 13, and we therefore obtain the value

$$\Delta \mathbf{E} = t_C \cdot 0.05915 \log \gamma m/(Cl^-) \qquad (14)$$

to be added to the values of $\mathbf{E}_0$. The cation transference number (t_C) is taken as 0.828.[13] The values of $\Delta \mathbf{E}$ are given in the sixth column of Table III, and the corrected values of $\mathbf{E}_0$ in the seventh column. The values of γm used in calculating $\mathbf{E}_0$ are given in the eighth column for comparison with those of (Cl^-).

TABLE III

CALCULATED VALUES FOR THE COPPER AMALGAM-CUPROUS CHLORIDE ELECTRODE

No.	m_{HCl}	$\mathbf{E}_0$	$\gamma_{Cu^{++}}$	(Cl^-)	$\Delta \mathbf{E}$	$\mathbf{E}_0'$	γm
1	0.02029	−0.13116	0.53	0.01731	0.0010	−0.1302	0.01813
2	.02029	− .13113	.53	.01731	.0010	− .1301	.01813
3	.00757	− .12915	.63	.00795	− .0026	− .1317	.00706
4	.00757	− .12907	.63	.00795	− .0026	− .1317	.00706
5	.03564	− .13116	.48	.02932	.0013	− .1299	.03115
6	.03564	− .13100	.48	.02932	.0013	− .1297	.03115

The calculated values of (Cl^-), as compared with γm, show that in the case of the most concentrated solution the effect of complex formation is

[12] See ref. 8, p. 337 and ref. 16, p. 782 (chapter by Harned).

[13] Partington, "Conductance, Ionization, and Ionic Equilibria," p. 546. Chapter XI of Taylor's "Treatise on Physical Chemistry," D. Van Nostrand Co., New York City, 1925.

predominant, while in the case of the most dilute solution the effect of formation of cupric chloride is predominant. This is qualitatively verified in the experiments. The experimental data show that the formation of cupric chloride did not take place to the extent calculated. This fact is somewhat surprising, considering the constancy and reproducibility of our electrodes. It might be mentioned that an error in the activity coefficient of Cu^{++} would have a marked effect on the calculated values of (Cl^-). We shall take the value of E_0' for the most concentrated solution, and regard this as the standard potential of copper amalgam and cuprous chloride in the presence of chloride ion at unit activity. This value is probably correct to within two- or three-tenths of a millivolt. We therefore write

Cu (in two-phase amalgam) $+ Cl^- = CuCl(s) + E^-$; $E^\circ = -0.1298$ volt,

$$\Delta F_{298}^\circ = 23074 \cdot 0.1298 \text{ cal.} = 2995 \text{ cal.} \quad (15)$$

This value is to be used in calculating free energies and equilibrium constants. The values of E_0 in Table III may be used when the electrode is employed as a reference electrode with a given hydrochloric acid solution.
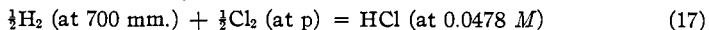
Our value for the standard potential of this electrode is to be compared with that of Noyes and Chow,[4] who found —0.1200 volt for the standard potential, using copper plated on platinum. The standard potential of the amalgam in copper sulfate, as found in our previous paper, is —0.3502 volt. Lewis and Randall give —0.3448 volt, based on the work of Lewis and Lacey,[14] for the standard potential of a copper sponge prepared by rapid electrolysis of copper sulfate on a platinum point. We have been unable to produce copper of as low reducing power as this by any method whatever, but this copper would give —0.1244 volt for the standard potential of the copper-cuprous chloride electrode. Comparison of this value with that of Noyes and Chow, ignoring the slight error introduced by the liquid junction, indicates that the smooth copper plate which they used contained energy stored in the form of distortion from a more stable form of copper.

Calculations: The Cuprous Chloride-Cupric Chloride Electrode

The reaction which occurs in the copper chloride cells (Table II) is

$$CuCl(s) + \tfrac{1}{2}Cl_2 \text{ (at p)} = CuCl_2 \text{ (at } m) \quad (16)$$
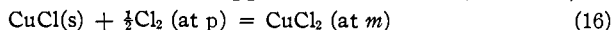
That which occurs in the hydrochloric acid cell is

$$\tfrac{1}{2}H_2 \text{ (at 700 mm.)} + \tfrac{1}{2}Cl_2 \text{ (at p)} = HCl \text{ (at 0.0478 } M) \quad (17)$$

The electromotive force that would be given by the latter cell if all substances were at unit activity is 1.3594 volts, according to the tables of Lewis and Randall, based on the work of Lewis and Rupert.[9] If only the chlorine were at a fugacity or activity of one atmosphere and the other substances at the concentrations indicated by Equation 17, the electromotive force would be

[14] Lewis and Lacey, THIS JOURNAL, **36**, 804 (1914).

$$1.3594 + 0.05915 \log \frac{(700/760)^{1/2}}{(0.861)^2(0.0478)^2} = 1.5222 \text{ volts}$$

the activity coefficient for the given hydrochloric acid being taken as 0.861 from Lewis and Randall. In order, therefore, to find the electromotive force that would be given by the copper chloride cells if the chlorine were at unit activity, the difference between the value 1.5222 and the observed value E_{HCl} (Table II) must be added to the corresponding value of E_{CuCl_2}, since the same chlorine mixture was used in the two corresponding cells. These corrected values E_0 for the copper chloride cells are given in the third column of Table IV, the first giving the number of the experiment and the second the molality of the cupric chloride used. The hydrolysis of the chlorine is negligible at the partial pressures used. The mean value of E_0 at each molality is given in the fourth column.

As in the case of our copper-cuprous chloride electrodes, the concentration of chloride ion is affected by the formation of $CuCl_2^-$ and, in the case of the more concentrated solutions, by the formation of much $CuCl_3^-$ and various chloro-cuprate ions. We shall neglect all factors except the formation of $CuCl_2^-$, although these factors are by no means completely negligible in the concentrated solutions. If we assume that the concentration of chloride ion is cut down by cuprous chloride in the ratio $1/1.0661$ in accordance with Equation 5, then the chlorine would become chloride ion at molality $2m_{CuCl_2}$ and the cuprous chloride would form chloride ion at molality $2m_{CuCl_2}/1.0661$. If all the transference were accomplished by positive ions, the chloride ions formed would remain at these molalities, and the value $0.05915 \log 1.0661$ would have to be subtracted from the values of E_0 in Table IV to find the e.m.f. that would be obtained if the concentration of chloride ion were really $2m_{CuCl_2}$. When the cell operates, however, some chloride ion is transferred from the chlorine electrode vessel to the cuprous chloride solution, which is more dilute with respect to chloride ion, and this has the effect of increasing the electromotive force by the amount $t_A \cdot 0.05915 \log 1.0661$, where t_A is the transport number of chloride ion. We are assuming a sharp boundary, as explained in the previous section, and a constant activity coefficient at any one molality. We must accordingly subtract the value

$$\Delta E = (1 + t_A)\, 0.05915 \log 1.0661 \tag{18}$$

from the values of E_0 to find the e.m.f. that would be obtained if the concentration of chloride ion were actually $2m_{CuCl_2}$. These corrected e.m.f.'s, E_0', are given in the seventh column of Table IV.

It might be argued that the $CuCl_2^-$ ion cannot be regarded as a foreign ion, since storing up an ion in the form of a complex might not be qualitatively different from storing it up as a hydrated ion or in any other unactivated form. In our treatment it is, of course, assumed that, of the total chloride ion present, the instantaneous fraction in active equilibrium

with solid CuCl and cuprous ion is reduced very nearly in the ratio $1/1.0661$ by complex formation.

In dilute solutions we shall take t_A as 0.6 by analogy with various electrolytes. In very concentrated cupric chloride solutions the transport numbers for the anion become greater than unity, owing to the formation of chloro-cuprate ions, according to the work of Kohlschütter.[15] Since we are regarding complex ions as foreign ions, our value of t_A must be the fraction of the current carried by the chloride ions alone, and we have selected the rather arbitrary values given in the fifth column of Table IV. This procedure ignores the fact that other ions are transferred to different environments, but the corrections are small and at any rate the presence of cuprous chloride makes the molalities and the calculated activity coefficient doubtful in the most concentrated solutions. The values of ΔE calculated from Equation 18 are given in the sixth column and the corrected values of E_0 in the seventh column, these corrected values, E_0', having the significance stated above.

From the reaction of Equation 16, the following relation must hold between the values of E_0'

$$E_{0x}' - E_{0y}' = 0.05915 \log \frac{(\gamma_y m_y)^3}{(\gamma_x m_x)^3} \qquad (19)$$

in which the x and y refer to the number of the experiment and $\gamma m = \sqrt[3]{(Cu^{++})(Cl^-)^2}$ where the parentheses denote activities. The "mean activity coefficient," γ, as calculated by Equation 19, is given in the eighth column of the table, that for the 0.01 molal solution being calculated from the table of individual ion coefficients of Lewis and Randall.

TABLE IV

CALCULATED VALUES FOR THE CUPROUS CHLORIDE-CUPRIC CHLORIDE ELECTRODE

No.	m_{CuCl_2}	E_0	Mean E_0	t_A	ΔE	E_0'	γ_{CuCl_2}
7	0.01	1.1328	1.1330	0.6	0.0026	1.1304	(0.700)
8	.01	1.1331					
9	.02	1.0889	1.0889	.6	.0026	1.0863	.620
10	.02	1.0889					
11	.2	.9523					
12	.2	.9520	.9523	.5	.0025	.9498	.365
13	.2	.9528					
14	1	.8368	.8367	.4	.0023	.8344	.326
15	1	.8365					
16	5.82[11]	.6605	.6605	.2	.0020	.6585	.55

Various causes may be given for the trend of the activity coefficient. The "electrostatic virial" theory of Debye and Hückel[16] as extended by Hückel[17]

[15] Kohlschütter, *Ber.*, **37**, 1153 (1904).

[16] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923). See also Noyes, THIS JOURNAL, **46**, 1080 (1924).

[17] Hückel, *Physik. Z.*, **26**, 93 (1925)

probably accounts for the greater portion of the trend. Scatchard[18] has suggested that hydration may be another factor in determining the values of γ. Many factors enter into consideration for the concentrated cupric chloride solutions, including hydration, formation of ionic and molecular complexes, etc. The factors are probably linked up with the color changes, the color changing from blue to green or from dark green to a dark reddish-brown on saturation with cuprous chloride, in the case of the most concentrated solutions. The molality, and hence the calculated activity coefficient, is somewhat in doubt in the case of the saturated solution, owing to the large solubility of cuprous chloride. Other complicating factors have been mentioned previously.

Since the cell reaction for this set of experiments is that given by Equation 16, we may calculate the standard potential of the cuprous chloride-cupric chloride electrode by the relation

$$E^\circ = E_0' + 0.05915 \log (Cu^{++}) (Cl^-)^2 + E_{Cl_2}^\circ \qquad (20)$$

using any value of E_0' and the corresponding values for the activities. This value, E°, is the value which, if the standard potential of the chlorine electrode be subtracted from it, gives the electromotive force that would be obtained from our cupric chloride cells if the activity of both ions were unity. Using the values for the 0.01 molal solution, including the "mean activity coefficient" of 0.700 and the standard potential of the chlorine electrode given previously, Equation 20 becomes

$$E^\circ = 1.1304 + 0.05915 \log 4(0.700 \cdot 0.01)^3 - 1.3594 \qquad (21)$$

We may therefore write

CuCl(s) = Cl^- + Cu^{++} + E^-; E° = -0.5758 volt,

$$\Delta F_{298}^\circ = 23074 \cdot 0.5758 = 13,285 \text{ cal.} \qquad (22)$$

This value, as well as our activity coefficients, is slightly in doubt, owing to the calculation of γ at 0.01 M from individual ion coefficients. The values of E_0 may be employed when this electrode is used as a reference electrode.

Standard Free Energies Based on Both Electrodes

Subtracting the standard chlorine potential from Equation 22, we obtain

CuCl(s) + $\frac{1}{2}Cl_2$(g) = $CuCl_2$ (aq. at unit activity)

$$\Delta F_{298}^\circ = -(1.3594 - 0.5758)23074 = -18,080 \text{ cal.} \qquad (23)$$

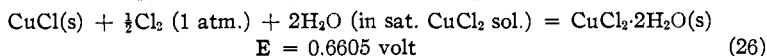Subtracting the standard potential of chlorine from Equation 15, we obtain

Cu (in two-phase amalgam) + $\frac{1}{2}Cl_2$(g) = CuCl(s)

$$\Delta F_{298}^\circ = -(1.3594 - 0.1298)23074 = -28,370 \text{ cal.} \qquad (24)$$

Combination of Equations 23 and 24 gives

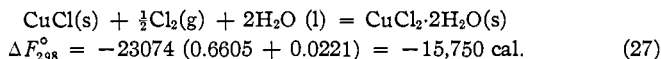Cu (in two-phase amalgam) + Cl_2(g) = $CuCl_2$ (aq. at unit activity)

$$\Delta F_{298}^\circ = -46,450 \text{ cal.} \qquad (25)$$
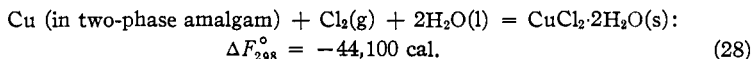
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[18] Scatchard, THIS JOURNAL, **47**, 2096 (1925).

From the value of E_0 for the saturated cupric chloride solution we may obtain the free energy of the dihydrate. The equation is
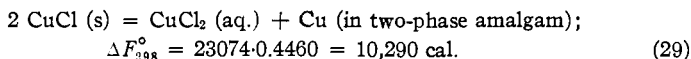
$$CuCl(s) + \tfrac{1}{2}Cl_2 \text{ (1 atm.)} + 2H_2O \text{ (in sat. } CuCl_2 \text{ sol.)} = CuCl_2 \cdot 2H_2O(s)$$
$$E = 0.6605 \text{ volt} \tag{26}$$

From the vapor-pressure data of Ewan and Ormandy,[19] the activity of the water is found to be 0.65. Hence the value $0.05915 \log (0.65)^2$, or -0.0221, has to be subtracted from Equation 26, and we obtain

$$CuCl(s) + \tfrac{1}{2}Cl_2(g) + 2H_2O \text{ (l)} = CuCl_2 \cdot 2H_2O(s)$$
$$\Delta F^{\circ}_{298} = -23074 \, (0.6605 + 0.0221) = -15,750 \text{ cal.} \tag{27}$$

Combination with Equation 24 gives

$$Cu \text{ (in two-phase amalgam)} + Cl_2(g) + 2H_2O(l) = CuCl_2 \cdot 2H_2O(s):$$
$$\Delta F^{\circ}_{298} = -44,100 \text{ cal.} \tag{28}$$

From Equation 9,

$$2 \, CuCl \text{ (s)} = CuCl_2 \text{ (aq.)} + Cu \text{ (in two-phase amalgam)};$$
$$\Delta F^{\circ}_{298} = 23074 \cdot 0.4460 = 10,290 \text{ cal.} \tag{29}$$

Summary

By measurements of the cell Cu (in two-phase amalgam), CuCl(s), HCl, H$_2$, the standard potential of the copper amalgam-cuprous chloride electrode was determined (Equation 15). The results were compared with those of other investigators.

By measurements of the cell Cl$_2$ (at low pressures), CuCl$_2$ (aq.), CuCl(s), the standard potential of the cuprous chloride-cupric chloride electrode was determined (Equation 22), as well as the activity of cupric chloride over a limited range (Table IV).

To insure reliable results, copper amalgam was used instead of metallic copper, oxygen was excluded and the electrodes were rotated in the thermostat. Chemical reactions affecting the concentration of chloride ion were treated mathematically and corrections made for them. Views regarding the liquid junctions and the trend of the activity coefficients were expressed.

The standard free energies of the two solid chlorides and of aqueous cupric chloride were calculated (Equations 24, 25 and 28) as well as the standard free energies of several other reactions.

LINCOLN, NEBRASKA

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[19] Ewan and Ormandy, *J. Chem. Soc.*, **61**, 775 (1892).